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DEPENDENCE OF THE HYDROGEN PERMEABILITY COEFFICIENT IN GLASSES OF THE SODIUM-SILICATE SYSTEM ON THE SILICA MODULUS

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The system $Na_2O – SiO_2$ used in designing compositions for producing gas microcontainers (microspheres) is investigated. Based on a known equation, an expression is obtained for the dependence of the hydrogen permeability coefficient of glass on its silica modulus. It is established that the alkaline modifier even in the form of an impurity can influence gas permeability. A conclusion is made on the need to apply criterial valuations in designing glasses. A nomogram is obtained for determining the silica modulus, hydrogen permeability coefficient, phase composition, and probability of glass formation in the $Na_2O – SiO_2$ system.

Hydrogen permeability is not a property traditionally considered in glass technology. The lack of detailed information is due to the fact that the application area of these products is mainly restricted to experiments in plasma physics, in which glass microspheres are used as microcontainers filled by a deuterium – tritium mixture. However, despite limited possibilities, technological problems call for solutions. The present study describes the results of studying the dependence of the hydrogen permeability coefficient in glasses on silica modulus.

The coefficient of hydrogen permeability $K_H \left[\dfrac{mole \cdot m^2}{m \cdot sec \cdot Pa} \right]$ and the silica modulus n_{Si} were calculated based on the formulas [1, 2]

$$K_H = 8.1 \times 10^{-14} \exp\left[-\frac{1}{T}(17{,}330 - 127.8C) \right]; \quad (1)$$

$$n_{Si} = \frac{x_{SiO_2}}{x_{Na_2O}}, \quad (2)$$

where x is the content of oxides, % (here and elsewhere molar content); T is the temperature, K; C is the sum of the glass-forming agents ($x_{SiO_2} + x_{B_2O_3} + x_{P_2O_5}$).

Correlation-regression analysis of the dependence of hydrogen permeability coefficient on the silica and borosilicate moduli, the structure cohesion factor, the oxygen number, and relative molar volumes of components was earlier performed for 23 borosilicate glasses [3]. High correlation coef-

ficients corroborated the advisability of using the specified structure-determining criteria for studying hydrogen permeability. Later the database of glass compositions was expanded and similar dependences were investigated for 35 glasses [4] used for making microspheres (21 compositions) and for other purposes in the industry (14 compositions). A high correlation of criteria was observed as well. Finally, the database was expanded to 100 compositions using additional published data. The compositions selected were those resembling the "microsphere" compositions with respect to their general qualitative compositions and individual components. The proper "microsphere" group included 40 glasses: 27 borosilicate, 10 aluminosilicate, 2 silicate, and 1 aluminoborosilicate composition; Na_2O was used in all cases. Thus, glasses of the $Na_2O – SiO_2$ system were used most frequently for microsphere production, accordingly, this system was selected for a more detailed study.

Thus, let a glass consist of the glass-forming agent SiO_2 and the modifier Na_2O. Then, it is quite obvious that

$$x_{SiO_2} = 100 - x_{Na_2O}. \quad (3)$$

We express x_{SiO_2} using expression (2):

$$x_{SiO_2} = n_{Si} x_{Na_2O}. \quad (4)$$

After substituting equation (4) into expression (3) we obtain the equality

$$n_{Si} x_{Na_2O} = 100 - x_{Na_2O},$$

from which is follows that

$$x_{SiO_2} = \frac{100 n_{Si}}{n_{Si} + 1}. \quad (5)$$

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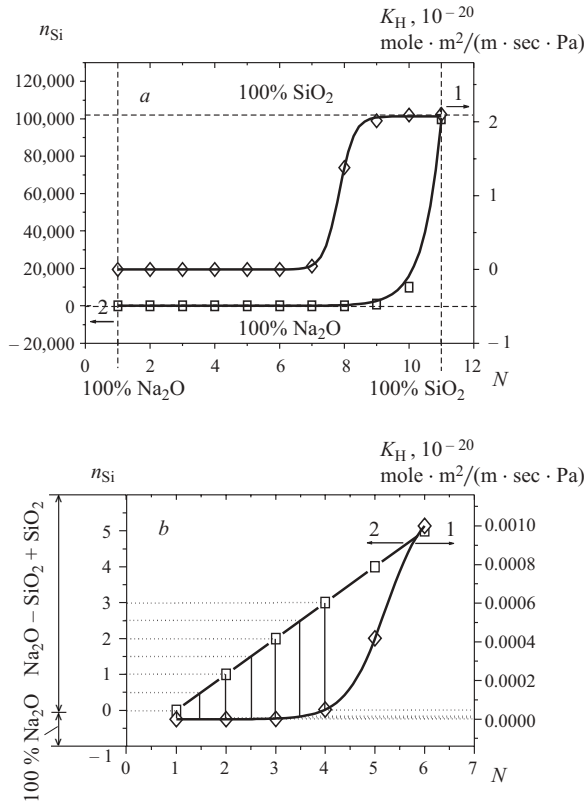
Fig. 1. Variation of silica modulus and hydrogen permeability coefficient in glasses of the system $Na_2O - SiO_2$ within the whole range of compositions including pure Na_2O and SiO_2 oxides (*a*) and within the composition range used in sol-gel technology (*b*).

Since only one glass-forming agent was used in the case considered, formula (1) can be written as follows:

$$K_H = 8.1 \times 10^{-14} \exp\left[-\frac{1}{T}\left(17{,}330 - 127.8 x_{SiO_2}\right)\right]. \quad (6)$$

Substituting expression (5) into Eq. (6), we obtain a formula for glasses of the $Na_2O - SiO_2$ system:

$$K_H = 8.1 \times 10^{-14} \exp\left[-\frac{1}{T}\left(17{,}330 - 127.8\,\frac{100 n_{Si}}{n_{Si}+1}\right)\right], \quad (7)$$

which explicitly proves the functional dependence of the hydrogen permeability coefficient on the silica modulus.

Setting different values of n_{Si}, the value of K_H was calculated based on Eq. (7) (Table 1, temperature taken equal to 300 K) and variation curves for the silica modulus and the hydrogen permeability coefficient were constructed (Fig. 1).

It follows from an analysis of the shape of the curves (Fig. 1*a*) and the data in Table 1 that the curve $K_H = f(N)$, in which N is the number of compositions, has a clearly expressed S-shape and belongs to the area limited by the lower limit $K_{H,\,min} = 6.62 \times 10^{-39}$ mole $\cdot$ m^2/(m $\cdot$ sec $\cdot$ Pa) at $n_{Si,\,min} = 0$ (the left vertical asymptote, 100% Na_2O) and the

TABLE 1

n_{Si}	K_H, 10^{-20} mole $\cdot$ m^2/(m $\cdot$ sec $\cdot$ Pa)	Main crystalline phase
0	6.62×10^{-19}	100% Na_2O
0.5	9.72×10^{-13}	Orthosilicate $2Na_2O \cdot SiO_2$
0.67	1.75×10^{-11}	Pyrosilicate $3Na_2O \cdot 2SiO_2$
1	1.18×10^{-9}	Monosilicate $Na_2O \cdot SiO_2$
2	1.43×10^{-6}	Disilicate $Na_2O \cdot 2SiO_2$
3	4.97×10^{-5}	$Na_2O \cdot SiO_2 + Na_2O \cdot 2SiO_2$
4	4.18×10^{-4}	
5	0.001	
10	0.043	$xNa_2O \cdot (100-x)SiO_2$, where $33.3 \geq x \geq 0$
100	1.38	
1000	2.01	
10,000	2.09	
100,000	2.1	

upper limit $K_{H,\,max} = 2.1 \times 10^{-20}$ mole $\cdot$ m^2/(m $\cdot$ sec $\cdot$ Pa) at $n_{Si,\,max} = 10^5$ (the right vertical asymptote, 100% SiO_2). Consequently, the S-shaped curve reflects variations of K_H of sodium silicates depending on their stoichiometric composition. At $n_{Si} = 7.5$ there is an inflection in the curve, then a sharp jump and the second inflection; and after $n_{Si} = 1000$ the curve starts monotonically approaching the upper limit of K_H.

This may have the following meaning: at $n_{Si} \geq 7.5$ structural modifications start that are related to completion of formation of a three-dimensional pure SiO_2 due to removal of the modifier impurity and two-dimensional structural patterns. The process continues up to $n_{Si} = 1000$ and ends when the sodium-silicate system smoothly transforms into a single-component system consisting only of the glass-forming component (the right vertical asymptote $n_{Si} = f(N)$ and the upper horizontal limit $K_H = f(N)$), It follows from the above that even a modifier impurity may have a perceptible effect on gas permeability; therefore, one should carefully design a quantitative composition of glass for gas microballoons and calculate the quantitative ratio between the components using the system of criterial estimates [3 – 9]. This will make it possible :

– to minimize the factor of indefiniteness in designing compositions, considering that the number of possible combinations of 83 chemical elements used in glass technology is infinite;

– to optimize material and power consumption;

– to extend the service life of machinery;

– to save working time of the technologist, etc.

Figure 1*b* shows a fragment of the curves in an interval of $1 \leq n_{Si} \leq 5$, in which synthesis of silicates by sol-gel technology is possible. Based on our own experience we note that synthesis in an aqueous medium easily proceeds at $n_{Si} \leq 3.4$ [7]; the composition range in this case belongs to the area indicated by solid vertical lines. The results of the dependence $n_{Si} = f(N)$ can be well approximated by a linear function, similarly to the results of $K_H = f(N)$ for the chosen

interval of silica modulus variation. Thus, a monotonic variation of the modulus in the range of $0 \leq n_{Si} \leq 3.4$ corresponds to a similar monotonic variation of the permeability coefficient. This corroborates the appropriateness of using the linear function $\log K_H = f(\log n_{Si})$ for calculation of glass-forming compositions [7]. The arrows to the left of the coordinate field indicate the ranges of 100% content of Na_2O, silicates of different compositions, and the direction increasing content of the glass-former (SiO_2). The dashed lines indicate the method for determining n_{Si} and K_H if one of these values is specified.

Taking into account these results and the data in [5], a nomogram was constructed for determining n_{Si}, K_H, the principal phase composition, and the ranges of more probable (+) and less probable (–) glass formation in the $Na_2O - SiO_2$ system (Fig. 2).

Conditions for glass formation in the $Na_2O - SiO_2$ system are unfavorable when the main phases are $2Na_2O \cdot SiO_2$ and $3Na_2O \cdot 2SiO_2$, which form isolated fragments and two-member chains of limited length [5], since the absence or shortage of bridge oxygen prevents the formation of bonded two-dimensional and three-dimensional lattices. Patterns with a sufficient quantity of bridge oxygen ions emerge in the cases of $Na_2O \cdot SiO_2$ and $Na_2O \cdot 2SiO_2$; therefore, a boundary vertical line indicated by arrows "–" and "+" is drawn between the second and the third point of the curve $\log K_H = f(\log n_{Si})$. Each point of the curve correlates with crystalline phases indicated in Fig. 2, which agrees with the data in [5]. The range near a point selected with particular values of $\log K_H$ and $\log n_{Si}$ means the formation of a mixture of phases from two neighboring points. An upward direction toward the upper limit points to the formation of silicates rich in silica, and approach to the boundary horizontal line means probable formation of SiO_2 in a free state. With $\log n_{Si} = 3$ a composition can be regarded as virtually one-component. In the same way, a direction toward the lower limit indicates synthesis of silicates rich in the modifier and relevant modifications of the modulus and the permeability coefficient. When the dimensionality of the structure decreases due to a decrease in the silica modulus, one can expect a decrease in the hydrogen permeability of the composition designed, and vice versa.

Thus, using glasses of the $Na_2O - SiO_2$ system by way of example, it has been demonstrated that hydrogen permeability characterized by the hydrogen permeability coefficient
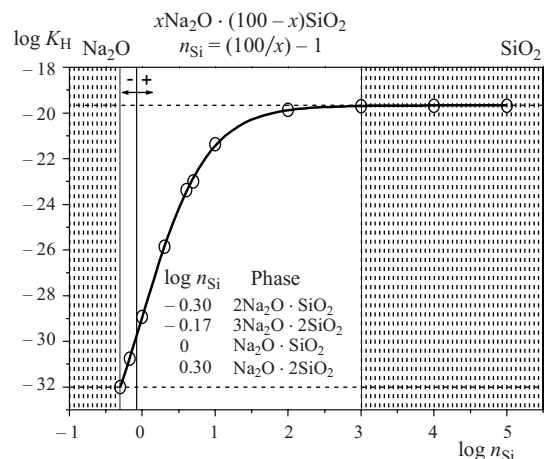

Fig. 2. Nomogram for determining silica modulus and hydrogen permeability coefficient, phase composition, and probability of glass formation in $Na_2O - SiO_2$ system.

directly depends on the silica modulus. This is due to the formation of sodium silicates of a certain stoichiometric composition and a specific type of glass structure.

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